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(54) Title: METHOD FOR COATING PARTICULATED FERTILIZERS (57) Abstract <p>The present invention relates to a method for coating particulated fertilizers like complex nitrogen-, phosphorus- and potassium fertilizer (NPK), nitrogen- and potassium type fertilizer (NK), ammonium nitrate fertilizer (AN), calcium nitrate fertilizer (CN) or urea to reduce dust formation and caking during handling and storage. The method comprises applying an aqueous solution of a mineral acid, such as phosphoric acid, sulphuric acid, nitric acid or citric acid and a mineral base, such as magnesium oxide, calcium oxide, barium oxide, dolomite or a mixture of two or more. Said combined treatment is performed only once to form a nutrient containing shell of a metal salt or mixture of metal salts on the particulate fertilizer. The ratio between said acid and said base applied onto the particulated fertilizers is between 1.0 to 1.5 weight/weight. It is feasible to add colour pigments and micronutrients to the shell.</p>		

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"Method for coating particulated fertilizers"

The present invention relates to an improved, cost competitive and environmental friendly method for coating particulated fertilizers like NPK, NK, AN, CN or urea to reduce dust formation and caking during handling and storage. The method comprises applying an aqueous solution of mineral acid, such as phosphoric acid, sulphuric acid, nitric acid or citric acid and a mineral base, such as magnesium oxide, calcium oxide, barium oxide, dolomite or a mixture of two or more onto the individual particulated fertilizers. Said combined treatment is performed only once to form a nutrient containing shell of a metal salt or a mixture of metal salts on the particulated fertilizer.

It has been known for a long time that particulated fertilizers like NPK (complex nitrogen-, phosphorus- and potassium fertilizer), NK (nitrogen- and potassium type fertilizer), AN (ammonium nitrate), CN (calcium nitrate) or urea give problems during storage and handling.

One problem which arises is the caking of the particulated fertilizers that can be caused by post reactions or plasticity of the fertilizer.

Furthermore, the particulated fertilizers have an ability to absorb humidity which may increase the caking tendency of the fertilizers. This will always lead to dust formation during storage and handling.

Another problem, especially during handling of the particulated fertilizers, is dust formation. There can be several reasons for this dust formation, for instance that the fertilizer particles are uneven. Due to the abrasion the particles are exposed to during handling, this roughness will wear off, and thereby form dust. Powder, normally used as an anticaking agent may wear off as well.

Fertilizers are to an increasing extent transported in bulk, and this results in large mechanical wear on the surface of the fertilizer particles. The mechanical wear may cause formation of refuse, i.e. large pieces are broken off the particles, and in addition there will be fine dust from the powder mentioned above. It is especially the fine dust particles which remain floating in the air for some time, which result in the unpleasant fly dust.

In addition, the environmental regulation regarding dust formation during loading and unloading requires a solution of the problem.

Several coating agents for different types of fertilizers, like mineral oil (e.g. Technical White Oil (TWO)), waxes, surfactants (e.g. amines) and synthetic polymers, have been developed for limiting or suppressing these problems. These conventional coating agents, however, contain compounds which can be harmful to the environment. TWO and the waxes, for instance, may contain carcinogenic compounds and some amines may form nitrosamines. Polymers and waxes have low biodegradability.

FR Patent No. 2686861 describes a coating procedure which substitutes the traditional coating with sealing of the particulated fertilizers by a solid capsule. It provides the fertilizers with a better protection and prevents it more efficiently from caking than a traditional coating does. The coating procedure is carried out by spraying the particulated fertilizers with a first reagent in the form of a mineral base, such as magnesium, calcium or barium oxide, followed by an aqueous

solution of a second reagent, such as phosphoric, sulphuric, nitric or citric acid which reacts with the first reagent to form a solid capsule of a metal salt. The application of the base and the acid has to be repeated twice to form the solid capsule. This capsule amounts to 1-10 % by weight based on the total weight of the fertilizer.

From US Patent No. 3392007 it is further known a method to form a coating of magnesium ammonium phosphate onto particulated fertilizers, primarily urea, by applying an aqueous solution of phosphoric acid and a mixture of magnesium oxide and ammonium phosphate onto the fertilizers to manufacture a water-proof, slow release urea fertilizer. This application is repeated so as to form successive layers of magnesium ammonium phosphate coatings on each of the urea particles. The total amount of added coating material of this slow release coating is 25-60 % by weight based on the total weight of the fertilizer.

The main object of the present invention was to arrive at an improved, cost competitive and environmental friendly method for coating particulated fertilizers like NPK, NK, AN, CN or urea to reduce dust formation and caking during handling and storage.

Another object of the present invention was to arrive at a method for coating particulated fertilizers like NPK, NK, AN, CN or urea to form a coating only consisting of nutrients.

A further object of the present invention was to arrive at a method for coating particulated fertilizers like NPK, NK, AN, CN or urea where it was feasible to add colour pigments directly to the coating during the coating procedure.

Furthermore, it was an object of the invention to arrive at a method for coating particulated fertilizers like NPK, NK, AN, CN or urea where it was feasible to add micronutrients directly to the coating during the coating procedure.

The inventors found that the problems mentioned above could be solved by coating each of the particulated fertilizers with a shell which should adhere to the particle itself. The coating procedure was carried out by first applying a mineral acid to the particulated fertilizers and secondly apply a mineral base to the fertilizers.

Depending on the chemical composition of the fertilizer, different chemical substances will be formed in the shell during the coating process. This is due to the reaction of the acid with the surface of the particulated fertilizer prior to the addition of the mineral base. The inventors have observed on X-ray-diffraction (XRD) that the shell consists of a metal salt or a mixture of metal salts such as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Mg}(\text{NH}_4) \cdot 2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and amorphous magnesium phosphate, which is only slightly or non-soluble in water. The shell is porous and does not delay the dissolving of the fertilizer.

The present invention will thus in its widest scope comprise a method for coating particulated fertilizers like complex nitrogen-, phosphorus- and potassium fertilizer (NPK), nitrogen- and potassium type fertilizer (NK), ammonium nitrate fertilizer (AN), calcium nitrate fertilizer (CN) or urea to reduce dust formation and caking during handling and storage of the fertilizer, by applying an aqueous solution of a mineral acid such as phosphoric acid, sulphuric acid, nitric acid or citric acid and a mineral base comprising magnesium oxide, calcium oxide, barium oxide, dolomite or a mixture of two or more of these components onto the individual particulated fertilizers, comprising that the particulated fertilizer first is treated with said acid and then with said mineral base and that said combined treatment is

performed only once to form a nutrient containing shell of a metal salt or a mixture of metal salts on the particulated fertilizer.

The preferred ratio between said acid and said base (calculated as metal oxide) applied onto the particulated fertilizers is between 1.0 to 1.5 weight/weight.

Another embodiment of the invention is that colour pigments are added the aqueous solution of the mineral acid before applying said solution onto the particulated fertilizers.

A further embodiment of the invention is that micronutrients as Co, Cu, B, Se or Fe either are added to the mineral acid before applying the aqueous solution of the acid onto the particulated fertilizers or admixed with the mineral base prior to its application.

The inventors found that the order of the reagents applied was of vital importance for the result considering dust formation, caking tendency and adherence to the particulated fertilizer. The best result was achieved when the acid was applied first, not the oxide as described by the above French patent. The inventors found that especially the dust formation was substantially lower when the acid was applied prior to the base.

Though, the US Patent No. 3392007 describes a coating method where the acid is applied prior to a mixture of magnesium oxide and ammonium phosphate, the latter has to be added to secure that the amount of magnesium ammonium phosphate formed is not less than about 7 % by weight based on the total weight of the fertilizer having a coating of 25-60 % by weight totally. This is important in order to prevent the coating to break away from the fertilizer composition itself.

Contrary to this, the inventors found that it is not necessary to add ammonium phosphate to the particulated fertilizers for preventing shell breakage since sufficient ammonium is already available in the basic fertilizer for forming required ammonium phosphate to obtain strong adherence of the formed shell to the particulated fertilizer.

The inventors also found that only one application of each reagent was needed, not three or more applications as taught by the above mentioned patents.

The ratio between the mineral acid and the mineral base applied onto the particulated fertilizers was also important for the results. The best results considering dust formation and caking tendency were achieved when the ratio between mineral acid and mineral base (calculated as metal oxide) applied was between 1.0 to 1.5 weight/weight (w/w).

Furthermore, the inventors found that the concentration of acid and mineral base shall be as low as possible. These two features are of great importance considering improved effects and minimising the coating costs.

The inventors found that it is feasible to add colour to the shell by adding pigments to the aqueous solution of the mineral acid instead of doing this at an earlier stage in the process of manufacturing the fertilizer.

Furthermore, the inventors found that it is feasible to add micronutrients as Co, Cu, B, Se and Fe to the shell by dissolving them in the mineral acid or admixing them to the mineral base prior to the coating process.

The coating process consists of adding only one acid and only one base to the particulated fertilizers. However, it is possible to use a post conditioning agent to further suppress the dust formation. A post conditioning agent as rapeseed oil,

sunflower oil, soya been oil or an other vegetable oil can be used. These oils are not harmful to the environment and are considered as nutrients as well.

The invention will be further explained and envisaged in the following examples.

Example 1

NPK 17-17-17 was produced to bulk in a fertilizer plant running at full capacity. The particulated NPK-fertilizer was coated by a method according to the invention.

The NPK-fertilizer was coated in a coating drum. The residence time of the particulated fertilizers in the coating drum was about 2.5 minutes. The coating procedure was carried out by spraying an aqueous solution of phosphoric acid onto the individual particulated fertilizers in amounts necessary for securing that the fertilizers are wet with acid, followed by applying to the wet fertilizers powder of magnesium oxide. The phosphoric acid and MgO were respectively applied only once to the particulated fertilizer in the drum. The chemical reaction was finished at the outlet of the drum. The temperature increase due to the exothermic reaction was about 8°C.

The set point for the phosphoric acid (52% P ₂ O ₅ industrial quality) was	:	1.1 - 1.15%
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The set point for the magnesium oxide (MgO) was	:	0.8 - 1.1%
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The mean value, based on the weight of the fertilizer, for the production was	:	H ₃ PO ₄ : 1.13%
		MgO : 0.84%

The total weight of the shell or coating was amounted to 1-5% based on the weight of the fertilizer. During the coating period test run samples were collected for testing in the laboratory.

The results from these test are as follows:

Caking tests at humid atmosphere:

Spot samples were mixed together, and samples for the laboratory tests were drawn from this mixture. These are referred to as assembly samples. The tests are performed at a pressure of 1 kg/cm² for 24 hours at 60% RH (relative humidity) and +25°C.

The results of these tests are shown in Table 1.

Table 1:

Assembly samples:

Sample	A			B			C		
1	710	710	760	840	980	1.000	2.640	2.370	2.370
2	620	640	690	940	980	1.000	2.310	2.550	2.430
3	640	690		880	990	960	2.400	2.370	2.490
Average	683			952			2.437		
Stand. deviation	47			57			105		

where A = particulated fertilizer with coating according to the invention
 B = particulated fertilizer with conventional coating (comprising wax, polymer, surfactant and oil)
 C = uncoated particulated fertilizer

The coating according to the invention has 28% lower caking tendency than the conventional coating and gives 72% protection against absorption of humidity compared to uncoated fertilizers. The conventional coated product gave 61% protection.

Penetration tests:

The penetration of water vapour through fertilizers placed in 1000 ml glasses was performed at 60 - 80% RH (relative humidity) at +25 °C for 9 days.

The results of these tests are shown in Table 2.

Table 2: Penetration of water (cm) vapour through fertilizer samples

A	B	C
5.7	9.2	11.6

There is a reduction of 38% of water penetration through the fertilizer, it means 38% less of product is damaged.

Dust:

A sample of the fertilizer is placed in a tube and tilted back and forward 20, possibly 40 times. This test simulates wear during bulk transport. The results of the test are shown in Tables 3 and 4.

"Main dust" means dust which is released after one minute in a fluidizing apparatus and is the dust which is in the fertilizer. "After abrasion dust" means dust formed during wear of the particulated fertilizer surface subsequent to the tilting test.

Table 3: Dust analysis after 2 weeks after production:

Assembly samples	Dust mg/kg		
	Main dust	After abrasion	Sum
A	100	130	230
A	40	98	138
A	32	54	86
Average	57	94	151
B	14	24	38
B	18	54	72
B	16	44	60
Average	16	41	57
C	40	182	222
C	46	188	234
C	38	194	232
Average	41	188	229

6 weeks after production (Table 4) the tests were repeated, and the dust was now equal and low both for the coating according to the invention and the conventional coating (respectively 72 mg dust/kg fertilizer and 74 mg dust/kg fertilizer). Values below 200 mg/kg are normally acceptable for handling.

Table 4: Dust analysis after 6 weeks after production:

Assembly samples	Dust mg/kg		
	Main dust	After abrasion	Sum
A	52	24	76
A	36	22	58
A	50	32	82
Average	46	26	72
B	36	32	68
B	26	48	74
B	28	52	80
Average	30	44	74
C	34	64	98
C	42	62	104
Average	38	63	101

X-ray diffraction:

Samples were taken of the produced coated fertilizers according to the invention and analysed both as bulk and as surface deposit. For the surface deposit analyses, the samples were rubbed between two wire cloths. The scraped off particles were finely ground in an agate mortar and mounted on a Si plate. The bulk samples were finely ground and mounted on a circular sample holder. All samples were analysed by X-ray diffraction. In the surface of the coated fertilizer the following substance was detected: $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (schertelite).

If water is absorbed there will be a hydrolysis to $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and MAP (Mono-Ammonium Phosphate).

There is no MgO or $\text{Mg}(\text{OH})_2$ left, accordingly all the added MgO has reacted. The reason for this is that the chemical reactions between the two coating components have come to a completion.

Example 2

The following four acids: phosphoric acid, citric acid, sulphuric acid and nitric acid have been tested in the laboratory together with: MgO , CaO , BaO , Dolomite and a mixture of oxides $\text{CaO}+\text{MgO}+\text{Dolomite}$ (= "Filterdust").

The concentrations (w/w) for the different components in the tests are as follows:

Test	Mineral Acid	Mineral base
D =	1.1 % H_3PO_4 +	1.0 % MgO
E =	1.1 % H_3PO_4 +	1.0 % CaO
F =	1.1 % H_3PO_4 +	1.4 % Filterdust
G =	1.0 % Citric acid +	1.5 % MgO
H =	1.0 % H_3PO_4 +	1.5 % BaO
I =	1.0 % H_2SO_4 +	1.4 % "Filterdust"
J =	1.0 % HNO_3 +	1.0 % MgO
K =	1.1 % H_2SO_4 +	1.0 % CaO
L =	1.0 % H_2SO_4 +	1.44 % Dolomite
M =	1.0 % H_3PO_4 +	1.44 % Dolomite

The tests were performed in the laboratory, and the coating took place in a coating drum. All tests were repeated twice. The fertilizer particles (NPK- fertilizer) were heated to 30°C prior to the coating operation. The results from the physical quality tests are shown below.

Caking tests at humid atmosphere:

The caking tests were performed as described in example 1.

Caking test at 60% RH and 25°C for 24 hours (pressure 1 kg/cm²)

Sample	D			E			F		
1	1.550	1.250	1.220	2.040	2.610	2.670	1.290	1.350	1.740
2	860	1.340	1.590	1.740	1.800	2.070	1.650	1.500	1.350
Average	1.320			2.155			1.480		
Stand. deviation	265			398			183		

Sample	G			H			I		
1	810	600	810	1.530	920	780	750	930	450
2	510	870		300	990	1.200	390	360	450
Average	720			953			555		
Stand. deviation	156			413			231		

Sample	J			K			L		
1	2.040	1.440	1.890	1.890	2.040	1.920	1.440	2.460	1.440
2	1.890	1.290	1.680	1.590	2.220	1.860	1.950	1.290	2.760
Average	1.705			1.920			1.890		
Stand. deviation	291			209			555		

Sample	M		
1	1.710	2.580	1.050
2	1.290	1.320	1.290
Average	1.540		
Stand. deviation	504		

The test results show that the caking tendency is reduced by using the alternative coatings obtained by the method according to the present invention compared to conventional coating and uncoated fertilizer particles.

Dust:

The method used for these tests is another method than used in the previous example. It measures both the main dust (flydust) and the dust created during a 2 minutes abrasion in a glass column (abrasion dust). The dust values are not comparable to the values in the previous example since a different test method has been used. Dust tests have been performed for sample D, F, J and M.

Sample	Dust mg/kg
D	920
D	916
Average	918
F	1.059
F	1.309
Average	1.184
J	1.098
J	748
Average	923
M	488
M	460
Average	474

Values below 1000 mg/kg are normally acceptable for handling.

The test results show that the dust formation is acceptable for the coating obtained by the method according to the present invention.

Penetration tests:

The penetration of water vapour through fertilizer particles placed in 1000 ml glasses was performed at 60-80% RH at +25°C for 9 days. The results of these tests are shown in the table:

Water penetration

Sample	Swelling cm	Penetration cm
D	1	6.2
E	1	6.6
F	1	7.7
G	1.5	7
H	1	9
I	1	7.9
J	1	9.4
K	1	8.3
L	1	9.8
M	1	8.1

The test results show that the water vapour penetration through the fertilizer particle is reduced by using the alternative coatings obtained by the method according to the present invention compared to conventional coating as well as uncoated particles.

By the present invention the inventors have arrived at an improved, cost competitive and environmental friendly method compared to conventional methods for coating particulated fertilizers.

This is obtained by

- a) first applying the mineral acid, not the mineral base in excess
- b) only one base is added
- c) the mineral acid and the mineral base are added only once, respectively
- d) the total weight of the shell is quite small, only 1-5%, compared to the above known coatings
- e) the coating gives 28% lower caking tendency than the conventional coating
- f) there is a reduction of 38% of water penetration through the fertilizer, it means 38% less of product is damaged
- g) the dust formation is low and about the same for the coating according to the invention and the conventional coating (wax, polymer etc.), (respectively 72 mg dust/kg fertilizer and 74 mg dust/kg fertilizer), but substantially lower than for known inorganic coatings.

Claims

1. Method for coating particulated fertilizers like complex nitrogen-, phosphorus- and potassium fertilizer (NPK), nitrogen- and potassium type fertilizer (NK), ammonium nitrate fertilizer (AN), calcium nitrate fertilizer (CN) or urea to reduce dust formation and caking during handling and storage of the fertilizer, by applying an aqueous solution of a mineral acid such as phosphoric acid, sulphuric acid, nitric acid or citric acid and a mineral base comprising magnesium oxide, calcium oxide, barium oxide, dolomite or a mixture of two or more of these components onto the individual particulated fertilizers, comprising that the particulated fertilizers first are treated with said acid and then with said mineral base and that said combined treatment is performed only once to form a nutrient containing shell of a metal salt or a mixture of metal salts on the particulated fertilizers.
2. Method according to claim 1
characterised in that
the ratio between said acid and said base (calculated as metal oxide) applied onto the particulated fertilizers is between 1.0 to 1.5 weight/-weight.
3. Method according to claim 1,
characterised in that
colour pigments are added the aqueous solution of the mineral acid before applying said solution onto the particulated fertilizers.

4. Method according to claim 1,

characterised in that

micronutrients as Co, Cu, B, Se or Fe either are added to the mineral acid before applying the aqueous solution of the acid onto the particulated fertilizers or admixed with the mineral base prior to its application.